# Isoprene-butadiene-styrene pentablock copolymer and its preparation method


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Abstract of **CN1263119**

The present invention relates to an isoprene, butadiene and styrene pentablock copolymer and its preparation method. It possesses the following symmetrical structure: SBR-B-I-B-SBR, in which SBR is butaidne and styrene random copolymer block, I is polyisoprene block, B is polybutadiene block, and the ratio of SBR block and (B+I) block is 10/90-90/10 (weight ratio), and the ratio of B and I is 10/90-90/10 (weight ratio).

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# ISOPRENE-BUTADIENE-STYRENE PENTABLOCK COPOLYMER AND ITS PREPARATION METHOD


## Abstract

The present invention relates to an isoprene, butadiene and styrene pentablock copolymer and its preparation method wherein said block copolymer has the following symmetrical structure: SBR-B-I-B-SBR, in which SBR is a butadiene and styrene random copolymer block, I is a polyisoprene block, B is a polybutadiene block, and the weight ratio of butadiene and styrene random copolymer (SBR) block to poly(conjugated dienes) (i.e., the sum of polybutadiene block B and polyisoprene block I), SBR/(B+I), is 10/90-90/10; and the weight ratio of polybutadiene block B to polyisoprene block I of the poly(conjugated dienes), B/I, is 10/90-90/10.


## Claims

1. An isoprene, butadiene and styrene pentablock copolymer characterized in that said copolymer has the following symmetrical structure: SBR-B-I-B-SBR wherein SBR is a butadiene and styrene random copolymer block, I is a polyisoprene block and B is a polybutadiene block; the block copolymer has a number average molecular weight of from $5\times10^4$ to $35\times10^4$; the contents of the styrene and butadiene in the butadiene and styrene random copolymer SBR block are respectively from 10% to 50% and from 50% to 90% by weight; and the weight ratio of butadiene and styrene random copolymer (SBR) block to poly(conjugated dienes) (the sum of polybutadiene block B and polyisoprene block I), SBR/(B+I), is from 10/90 to 90/10; and the weight ratio of polybutadiene block B to polyisoprene block I of the poly(conjugated dienes), B/I, is from 10/90 to 90/10.

2. The block copolymer according to claim 1, wherein said block copolymer has a number average molecular weight of from $10\times10^4$ to $25\times10^4$.

3. The block copolymer according to claim 1, wherein the contents of the styrene and butadiene in the butadiene and styrene random copolymer SBR block are respectively from 15% to 35% and from 65% to 85% by weight.

4. The block copolymer according to claim 1, the weight ratio of butadiene and styrene random copolymer (SBR) block to poly(conjugated dienes) (the sum of polybutadiene block B and polyisoprene block I), SBR/(B+I), is from 30/70 to 70/30; and the weight ratio of polybutadiene block B to polyisoprene block I of the poly(conjugated dienes), B/I, is from 30/70 to 70/30.

5. The block copolymer according to claim 1, wherein the content of 1,2-polybutadiene in the butadiene and styrene random copolymer SBR block is from 6% to 80% by weight.

6. The block copolymer according to claim 5, wherein the content of 1,2-polybutadiene in the butadiene and styrene random copolymer SBR block is from 10% to 50% by weight.

7. The block copolymer according to claim 1, wherein the content of 3,4-polyisoprene in the polyisoprene block I is from 6% to 35% by weight.

8. The block copolymer according to claim 7, wherein the content of 3,4-polyisoprene in the polyisoprene block I is from 10% to 20% by weight.

9. The block copolymer according to claim 1, wherein the content of 1,2-polybutadiene in the butadiene block B is from 6% to 35% by weight.

10. The block copolymer according to claim 9, wherein the content of 1,2-polybutadiene in the butadiene block B is from 10% to 20% by weight.

11. A process for the preparation of an isoprene, butadiene and styrene pentablock copolymer SBR-B-I-B-SBR characterized in that: isoprene is charged to a non-polar hydrocarbon solvent in a reactor according to the proportion of the monomers; optionally a polar additives is charged depending upon the microstructure of polyisoprene, and the species and amount of the polar additives is dependent on the desired content of 3,4-polyisoprene block in the polyisoprene block; the concentration of the monomers is 10% to 20% by weight; said non-polar hydrocarbon solvent is a hydrocarbon solvent or a mixture of hydrocarbon solvents selected from the group consisting of non-polar aromatic hydrocarbon and non-polar aliphatic hydrocarbon; the solution is stirred so as to achieve an initialization temperature of 30°C to 80°C; after the initialization temperature is reached, a difunctional alkyl lithium is charged as an initiator, the amount of the difunctional alkyl lithium is dependent on the number average molecular weight of the block copolymer which generally ranges from $5\times10^4$ to $35\times10^4$; the difunctional alkyl lithium initiator is selected from a single difunctional alkyl lithium initiator or a mixture of several difunctional alkyl lithium initiators, and the difunctional alkyl lithium initiator generally is selected from the group consisting of bislithiums derived from dihalogenated alkanes and oligomeric bislithiums thereof, bislithiums of naphthalene, and bislithiums derived from diene compounds and oligomeric bislithiums thereof; after the isoprene is polymerized completely, a batch of conjugated diene monomers is charged to the reactor according to the proportion of the monomers; after the above conjugated diene monomer is polymerized completely, a batch of conjugated diene

monomers and styrenic monomers in a polar additive is charged to the reactor according to the proportion of the monomers, and the polar additive is selected from the group of consisting of a oxygen-, nitrogen-, sulfur-, or phosphorus-containing polar compound, a metal alkoxide or a mixture thereof, and the polar additive is used in an amount sufficiently to make the butadiene and styrenic monomers copolymerize randomly, depending upon the species of the polar additive employed; the preparation of SBR block is started; after the above the butadiene and styrenic monomers are polymerized completely, an anti-aging agent (1010 and 2.6.4 mixed in a weight ratio of 1:1) is charged in to the reactor; the polymer solution is then treated by conventional methods; after being dried, the resulting product is analyzed and tested and the pentablock copolymer SBR-B-I-B-SBR is obtained.

12. The process according to claim 11, wherein said bislithiums derived from dihalogenated alkanes and oligomeric bislithiums thereof are selected from LiRLi and Li(DO)nR(DO)nLi, wherein R represents an alkylene group having from 4 to 10 carbon atoms, DO represents a conjugated diene having from 4 to 8 carbon atoms or a mixtures of several conjugated dienes, n represents the oligomerization degree, ranging from 2 to 8.

13. The process according to claim 12, wherein said conjugated diene is selected from butadiene and isoprene and the oligomerization degree n is 3 to 6.

14. The process according to claim 11, wherein said bislithiums derived from diene compounds and oligomeric bislithiums thereof are selected from the group consisting of 1,1'-(1,3-phenylene)-di(3-methyl-1-(4-methylphenyl)pentyl)bislithium, 1,1'-(1,3-phenylene)-di(3-methyl-1-(4-methylphenyl)pentyl)butadiene oligomer-bislithium, 1,1'-(1,3-phenylene)-di(3-methyl-1-(4-methylphenyl)pentyl)isoprene oligomer-bislithium, 1,1'-(1,4-phenylene)-di(3-methyl-1-(4-methylphenyl)pentyl)bislithium, 1,1'-(1,4-phenylene)-di(3-methyl-1-(4-methylphenyl)pentyl)butadiene oligomer-bislithium and 1,1'-(1,4-phenylene)-di(3-methyl-1-(4-methylphenyl)pentyl)isoprene oligomer-bislithium.

15. The process according to claim 11, wherein bislithiums of naphthalene selected from the group consisting of dilithionaphthalene and α-methyl-dilithionaphthalene.

16. The process according to claim 11, wherein said non-polar hydrocarbon solvent is selected from the group consisting of benzene, toluene, ethylbenzene, xylene, pentane, hexane, heptane, octane, cyclohexane, mixed xylene and raffinate oil.

17. The process according to claim 16, wherein said non-polar hydrocarbon solvent is selected from the group consisting of hexane, cyclohexane and raffinate oil.

18. The process according to claim 11, wherein said oxygen-containing polar additive is selected from diethyl ether, tetrahydrofuran, R1OCH2CH2OR2 and R1OCH2CH2O CH2CH2OR2, wherein R1 and R2, being the same or different, each represents an alkyl having from 1 to 6 carbon atoms.

19. The process according to claim 18, wherein said oxygen-containing polar additive is selected from ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dimethyl ether and Ethylene glycol dibutyl ether and crown ether.

20. The process according to claim 11, wherein said nitrogen-containing polar additive is selected from triethylamine, tetramethyl ethylene diamine (TMEDA), and dipiperidino ethane (DPE).

21. The process according to claim 20, wherein said nitrogen-containing polar additive is selected from tetramethyl ethylene diamine (TMEDA).

22. The process according to claim 11, wherein said phosphorus-containing polar additive is selected from hexamethylphosphoramide (HMPA).

23. The process according to claim 11, wherein said metal alkoxides is selected from ROM, wherein R represents an alkyl having from 1 to 6 carbon atoms, O represents an oxygen atom, and M represents a metal cation sodium (Na) or potassium (K).

24. The process according to claim 11, wherein said metal alkoxides is selected from tert-butoxy potassium and tert-pentyloxy potassium.